EFFECT OF INERT GAS PRESSURE AND SOLUBILITY ON ELECTRICAL CONDUCTANCE OF FUSED $AgNO_3$

by

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LIST OF SYMBOLS

C	cell constant
D	self-diffusion coefficient
F	Faraday's constant
k	specific conductance; Boltzmann's constant
V_h	the most probable volume of a hole found in a melt
N_h	the molar density of holes in a melt
P	pressure
T	absolute temperature
c_i	concentration of ion i
d	density
K	Henry's law constant
E	energy of activation
m	mass
u_i	mobility of ion i
Λ	equivalent conductance
γ	surface tension
λ	ionic-equivalent conductance
z_i	charge on ion i
R	gas constant
L	effective length of cell
A	effective cross-section cell
C^*	concentration in units of equivalents per cm^3

INTRODUCTION

I. Purpose of this Investigation

There is very little known of the solubilities of the noble gases in various molten salts at high pressures, and there is not much information available in the literature as to the effects of the pressure and solubility of these gases on the conductances of molten salts. The purpose of this investigation was to help elucidate the physical nature of a fused salt which is saturated with a noble gas at high pressures; in particular, it was desired to obtain a better picture of conductance in fused salts, as well as to make available information as to how similar systems may be expected to behave. This work includes: (a) solubility measurements of argon and helium in molten silver nitrate at pressures from 100 to 450 atm at 250°; (b) conductance measurements of the fused silver nitrate at 250° under pressure of either argon or helium; and (c) an interpretation of the affects of the solubilities of the of the gases and pressures upon conductance of the salt. These aspects are compared with the similar work done by Zybko and Copeland on fused sodium nitrate. The resulting discussion will be in terms of the sizes of the solute gas atoms and their possible occupancy of some liquid free volume or holes in the melt, and the possibility of "dilution" of the fused salt due to gas molecules creating holes in the melt.

II. Solubility

The solubility of a gas in a liquid has a definite value, depending upon the natures of the liquid and the gas, temperature, and pressure. Let us consider a solution of a molten salt and a gas where the melt acts as the solvent and the gas is the solute. If the solution is very dilute, the solute molecules of gas are effectively completely surrounded by the molecules of solvent. The solute is then in a uniform environment irrespective of the fact that the solution may be far from ideal at higher concentrations.

In such a very dilute solution and at constant temperature, the gas's solubility in its uniform environment is proportional to the pressure of the gas in equilibrium with the solution. Thus, if $\underline{m}$ is the mass of gas dissolved by a definite volume of solvent at the equilibrium pressure $\underline{P}$, then we have the following equation, where $\underline{K}$ is Henry's law constant

$$\underline{m} = \underline{K}\,\underline{P} \qquad \text{(Henry's Law)} \qquad 1$$

The above equation, 1, may be expressed in another way. The mass, $\underline{m}$, of gas dissolved per unit volume of solvent is really the concentration of g cm^{-3}, and this is proportional to the concentration of the solute expressed in moles per liter of solvent, or per liter of solution since in a dilute solution only insignificant volume changes occur when the gas dissolves. The pressure, $\underline{P}$, of the gas is proportional to the number of moles per liter (or concentration) of the gas above the liquid. Thus, if we rearrange equation 1 we obtain the following

$$\underline{K} = \underline{m}/\underline{P} \qquad 2$$

$\underline{K}$ is a constant which can also be expressed generally as

$$K = \frac{\text{concentration of gas in the liquid phase}}{\text{concentration of gas in the gaseous phase}} \qquad 3$$

III. Conductivity

Information relating to the nature of ions present, the nature of the ionic conductance process, and the structure of a melt can be obtained from measurements of the variation of electrical conductance with various parameters such as the pressure and temperature (1).

The specific conductance, k, at a particular temperature, t, of a system is related to the resistance, R, by the following expression

$$k_t = C/R \qquad 4$$

where C is the cell constant for the system, and

$$C = L/A \qquad 5$$

where L is the effective length of the conductance path and A is its effective cross-section. In practice, C is not geometrically calculated but is determined experimentally with a solution of known specific conductance.

A term, equivalent conductivity, Λ, was defined by Kohlrausch (34) by the following equation

$$\Lambda = 1000\ k_t/C_{eq} = k_t/C^* \qquad 6$$

where C^* is the concentration in units of equivalents per cm^3.

It can be shown that the specific conductance is determined by the concentration of each ionic species in the system, c_i, the charge on each ion, z_i, and the mobility of each ion, u_i (2,3). Thus, we have for specific conductance the following relationship

$$k_t = (F/1000) \sum c_i z_i u_i \qquad 7$$

By absorbing the Faraday constant, F, into the mobility term, the equation becomes with rearrangement (3)

$$1000\ k_t/c_i z_i = (\lambda \text{ anion} + \lambda \text{ cation}) \qquad 8$$

where λ anion, and λ cation are the equivalent ionic conductances of the anion and cation, respectively. The concentration term, c_i, is expressed in moles of solute per liter of solution. The expression

$$\underline{c}_i / 1000 \qquad 9$$

is in equivalents per milliliter. In our case of a pure molten salt which is fully dissociated, this latter term may replaced by $\underline{M}/\underline{d}$, the equivalent weight of the salt divided by its density, $\underline{d}$.

IV. Models for the Structure of Molten Salts

When an ionic salt melts an expansion of 10 to 20% in volume usually occurs. It is not yet known with certainty how this additional volume is distributed in the melt. This volume is sometimes referred to as the "free volume," and there have been several theories put forward to explain its distribution. The two theories which to date have had the most success are the hole theory and the liquid (cell) free volume theory (4).

The liquid (cell) free volume model originated from considerations of compressed gases (liquified) made by Zernicke and Prins (4). Here the free volume is small compared to the space occupied by the molecules. The cell in which a molecule spends most of its time possesses a certain free volume, which is the difference in volume of the cell, or cage, in which the molecule is free to move, and the volume of the molecule itself.

The hole theory (4), which originated with Altar (4) and was developed by Furth (4), is designed to describe the density fluctuations that take place in the melt, as is also the liquid (cell) free volume theory. In the solid the size of the hole or cage must be either the size of one of the characteristic elements of volume or some integral number of these elements. This limitation is due to the rigidity of the solid system. However, in the liquid the situation is much less restrictive. Since the elements have much more freedom for movement in the liquid system, the holes may now not only be of different sizes and shapes but also may move by means of a continuous drift. The most probable volume of the hole in the melt is (4)

$$\underline{V}_h = 0.68\ (\underline{k}\ \underline{T}/\gamma)^{3/2} \qquad 10$$

where γ is the liquid-vapor interfacial tension. The molar density of the holes is thus

$$\underline{N}_h = (\Delta\underline{V}/\underline{V}_h)$$

where $\underline{V}$ is the difference between the molar volume of the liquid and that of the hypothetical solid at the same temperature. The work for making the hole is approximately $4\pi\underline{r}^2\gamma$, (4) where γ is again the liquid-vapor interfacial tension.

There are many reasons why the first liquid (cell) free volume theory seems inferior to the hole theory. In ionic melts, such as salts, the cations and anions are not free to pack at random, since the strong interionic forces in the liquid insure local electroneutrality. Thus a uniform local loosening of the structure, relative to the solid, appears unlikely. Therefore, one could ascribe the expansion in going from a solid to a liquid to the creation of gaps or holes. X-ray work (5,6,7) has shown that for KCl there is no significant change of the interionic spacing between nearest neighbors, but that a small decrease does occur in the mean coordination number. This, of course, does not support the original liquid free volume model, which uses the idea of a general loosening up of the cell spacing, as compared to the hole theory where the free volume is comprised of holes.

It was also found that the activation energies for diffusion in molten NaCl are approximately one-tenth that of diffusion in the solid (8). It is assumed that the activation energy for this vacancy diffusion is the sum of the energy required to form a hole and the energy required for the particle to move from one site to the next. Since the activation energy is very small, this suggests that a large number of vacancies may already exist in the melt such that the activation energies observed for diffusion correspond mainly to the energy of activation for site-to-site jumping.

In a modified version of the liquid free volume model due to Cohen and Turnbull (9,10), the free volume is the difference between the volume of the liquid and that of the hypothetical solid at the same temperature. This modified theory proposes that above a certain temperature this free volume can be distributed in the liquid without any energy change, due to the compensating changes in the potential energy of the particles. That is "the increase in energy due to expansion of a particular cell should be just balanced by the energy decrease from the compensation of another cell" (11). This theory allows diffusive displacement of the system's particles when a void above a certain critical size appears adjacent to it. It is assumed that this void is just large enough to allow the ion to jump into it, and that after entering this new void another ion takes its place in the old site. These voids are considered to arise from the redistribution of the free volume found in the melt's structure. The term "free" is defined in this theory as that volume which can be redistributed without energy change. The equation derived by Angell (12) for the self diffusion coefficient, D, in this model is

$$D = A T^{\frac{1}{2}} \exp\left[-k/(T - T_o)\right] \qquad 12$$

where A and k are constants (k is not Boltzmann's constant), T_o is the temperature at which the free volume begins to appear (glass transition temperature in glass-forming melts), and T is the experimental temperature. Angell found that for $Ca(NO_3)_2 + KNO_3$ glass-forming melts, plots of log $(T^{\frac{1}{2}}/D)$ versus $1/(T - T_o)$ were linear (12). It should be noted here that Bockris, et al., (13) stated that although the above theory does explain the transport behavior in glass-forming melts, it does not do so in simple liquids. The hole theory predicts independence of the pre-exponential constant from temperature

$$D = A \exp(-E/RT) \qquad 13$$

where D is the diffusion coefficient, E is the energy of activation, R is the gas constant, T is the absolute temperature, and A is a term which is independent of temperature. Many salt studies(8,14-18) have been shown to obey the diffusion equation used in the hole theory.

EXPERIMENTAL

I. Chemicals

Reagent grade silver nitrate was obtained from Allied Chemical, Fisher Chemical, Mallinckrodt Chemical and Baker Chemical Companies. The samples were heated above their melting point to remove moisture. The salt was allowed to cool and to solidify in a porcelain casserole in a desiccator, then the salt was crushed and placed in a Pyrex liner-conductance cell. This cell was sealed in a 500-cc capacity Inconel metal bomb, which was pumped out at room temperature by a mechanical vacuum pump overnight to remove air and any additional moisture.

II. Apparatus

A. Commercial Equipment

A 500-ml capacity Inconel metal bomb, type A243HC5 of the Parr Instrument Company, was fitted, according to specifications by J. L. Copeland (30), with two Conak No. TG-20-A-2-1 thermocouple glands packed with "Lava," a natural magnesium silicate. A Super-Gauge, made by the U.S. Gauge Division of Ametek, was connected to the bomb. This gauge measures pressures to 8,000 p.s.i.g., and is calibrated in divisions of 100 p.s.i.g. The manufacturer claimed the accuracy of this gauge to be ± 40 p.s.i.g., or slightly better than ± 3 atm. In the conductivity work one of the CONAX glands contained a chromel-alumel thermocouple, and the other contained a pair of 20-gauge platinum wires for conductance electrodes. The thermocouple was protected by a Pyrex tube. For solubility measurements, the platinum wires in the one gland were replaced by a 20-gauge chromel-alumel thermocouple. The accuracy of each of the thermocouples was approximately $\pm 0.25^{\circ}$. In the conductance work, the thermocouple was approximately ½ inch from the lower end of the cell, at the same height as the platinum electrodes. On the other hand, during the solubility study, the lower thermocouple was again about ½ inch from the bottom of the cell, while the upper thermocouple was about 1.5 inches from the top of the bomb, in the center of the gas phase. The bomb was sealed with a copper gasket which was seated in grooves provided in the head and cylinder of the bomb, and the bomb was held together by eight cap screws in a hardened steel band. A photograph of the entire bomb assembly is given in reference (19).

The vacuum pump used was a Cenco HYVAC No. 91105, .3 microns of Hg. When gas pressure higher than that in the gas cylinder was required, an Aminco air-operated, single-ended diaphragm type compressor, No. 46-4025, was used. This vertical unit consists of a six-inch single shaft air operator connected directly to a hydraulic plunger which transmits pressure to a hydraulic medium. The advantage of this type of compressor is that the gas to be compressed comes in contact only with a metal diaphragm and not with oil or water. Thus, no contamination of the gas is possible. One of the chromel-alumel thermocouple leads was connected directly to a Rubicon potentiometer No. 2703 with an internal standard cell, while the other lead went by way of a cold junction in an ice bath.

The conductivity measurements were made with an Industrial Instruments Company Conductance bridge, model RC-18. Shielded cable was used for all connections, and the bomb itself was electrically grounded, as was also the bridge.

B. Constructed Equipment

In both conductance and solubility experiments a Pyrex liner or liner-cell (20), as shown in reference (19), was used in the bomb to contain the salt, thus protecting the bomb from corrosion. In the conductance study the liner also was used to hold the conductance tubes rigidly. The liner was constructed from 6 cm tubing of length 15 cm to which a flat bottom was sealed. In the conductance work two 1-cm o.d. tubes extended to within ½ cm from the bottom of the liner. One of these tubes was tapered into a 2-mm i.d. capillary which was positioned horizontally in the form of an arc. The length of the capillary was about 6 cm. The thermocouple junction, conductance electrodes, and capillary all lay in the same horizontal plane to eliminate any vertical temperature gradient. A cover was made for the conductance cell from a 15 x 60-mm Petri dish with three 5-mm diameter holes blown out of the flat part.

Two furnaces were used in these experiments. One was made from a steel container, using a ¼ inch thick Transite cover with a hole drilled in it large enough to accomodate the top of a 4-inch i.d. aluminum oxide core, made by the Norton Company. The core was fixed vertically in the furnace housing. The outside of the core was wound with 18-gauge Chromel-A wire, used as the heating element. Alundum No. RA1055 refractory cement, made by the Norton Company, was placed over the outside of the wire-wound core. Super Stic-Tite asbestos cement served as insulation between the core and walls of the furnace. The temperature in the furnace was maintained by a 220-volt Powerstat and was monitored by a 0-5 amp a.c. ammeter. This apparatus was later replaced by a commercial Parr No. A404HC2 autoclave furnace.

III. Procedure

A. Solubility Determinations

The experimental procedure was adopted from that used by Zybko (19). Reagent grade silver nitrate was fused in a porcelain casserole to remove moisture and any other impurities. The salt was then allowed to solidify in a desiccator, after which the salt was crushed to a fine powder in a mortar with a pestle.

The Pyrex liner was cleaned first with soap and water, then was rinsed with distilled water and was cleaned again with concentrated nitric acid. The liner was cleaned until it shed distilled water. After cleaning, the liner was dried in an oven at 130° and cooled in a desiccator. The cell liner was charged with a weighed quantity of salt of about 350-500 g. to the nearest 0.5 g.

The charged liner was then placed in the bomb, after which the head was sealed on and the system was pumped out for about 12-14 hours to a pressure of .3 microns. The bomb was then charged with gas (either argon or helium) at room temperature to some desired pressure. The compressor was used if the desired pressure was higher than that in the supply cylinder. The bomb was allowed to stand at room temperature for about 1-3 hours to come to a temperature-pressure equilibrium within experimental error. After the equilibrium measurements of pressure and temperature were obtained, the bomb was heated to a salt temperature of 250° and the equilibrium gas pressure and gas temperature (which varied slightly from the salt temperature) were noted. The gas was then released and the system was disassembled. The salt, still in the molten state, was poured into a casserole and cooled in a desiccator to be used again. From the two pressure readings the solubility of the gas was determined.

For the solubility work it was necessary to determine the volume of the bomb. This value was taken as the average volume of the water needed to fill the sealed bomb, with all equipment inside. The water was added through a small orifice in the bomb's head which normally accomodated the pressure gauge. The average volume was 441.8 ± 1.0 cm^3. A correction facter of 2 cm^3 was added to this volume to account for the volume of the Bourdon tube of the pressure gauge.

B. Conductivity Measurements

The starting procedure employed for the solubility measurements was also used for determining the conductivity of the molten salt except that the platinum electrodes were in one of the glands. The bomb was first sealed and pumped out, and the salt in it was fused under vacuum and heated to 250°. After the value of conductance was determined under these conditions for the salt, the system was filled to 1 atm with the desired gas, and was allowed to equilibrate for about a day with frequent shaking. Once equilibrium was attained the conductance was again determined for the salt at 250°. This procedure was continued in steps of 500 to 1000 p.s.i.g. until about 6000 p.s.i.g. was achieved. The gas was then released and the system was allowed to equilibrate at 1 atm pressure with frequent shaking, and again the conductance of the system was determined. The bomb was then pumped out and the conductance under vacuum was determined for a second time. The system was opened and disassembled. The salt, poured into a casserole, was allowed to cool in a desiccator. Only new, fresh samples of silver nitrate were used for each conductance run.

RESULTS

I. Solubilities

The calculation of the solubility of argon or helium in silver nitrate was accomplished by subtracting the number of moles of gas remaining in the gaseous phase at 250° (salt temperature) from the number of moles of gas found in the gaseous phase at room temperature, where the salt was a solid. This difference in the number of moles of gas present in the gaseous phase was calculated by use of molar volume data for argon, and compressibility factor data for helium. For the argon solubilities, the molar volumes were obtained by interpolation and extrapolation of detailed plots of P-V-T data compiled by Din (21). For helium, compressibility factors were used, based on solutions of the Beattie-Bridgeman equation for a number of temperatures and pressures (22,23). Densities of the molten silver nitrate at 250°, $\underline{d}_{250}$, at various pressures were obtained from the following equation

$$\underline{d}_{250} = 3.920 + 4.9 \times 10^{-5} \, \underline{P} \text{ g cm}^{-3} \qquad 14$$

where pressure, $\underline{P}$, is in atm. This density-piston-pressure equation was obtained from the density-piston-pressure data of Owens (24). The determinations of the numbers of moles of gas were made using the gas temperature, which was found to be slightly lower than the salt temperature of 250°. Tables 1 and 2 contain a summary of the solubility data for the argon and helium solubilities, while Figures 1 and 2 are graphs of the solubilities of the two gases in the silver nitrate system.

TABLE 1. Summary of Solubility of Argon in Molten Silver Nitrate at 250°

Pressure, P_{Ar}, atm.	Solubility, C_{Ar}, mole cm^{-3} x 10^4	K_{Ar}, mole cm^{-3} atm, x 10^6
47	1.04	2.21
138	6.01	4.35
254	8.31	3.27
306	12.1	3.95
337	9.82	2.29
375	12.6	3.38
	Av. K_{Ar} = (3.35 ± 0.55) x 10^{-6} mole cm^{-3} atm^{-1}	

TABLE 2. Summary of Solubility of Helium in Molten Silver Nitrate at 250°

Pressure, P_{He}, atm.	Solubility, C_{He}, mole cm^{-3}, x 10^4	K_{He}, mole cm^{-3} atm^{-1}. c 10^6
51	2.20	4.32
73	2.52	3.46
79	2.70	3.42
96	2.90	3.02
215	7.30	3.39
247	9.37	3.79
	Av. K_{He} = (3.57 ± 0.48) x 10^{-6} mole cm^{-3} atm^{-1}	

Figure 1. Solubility of Argon in Molten Silver Nitrate at 250°, $\underline{C}_{Ar}$, $\underline{vs}$. Saturating Pressures of Argon, $\underline{P}_{Ar}$.

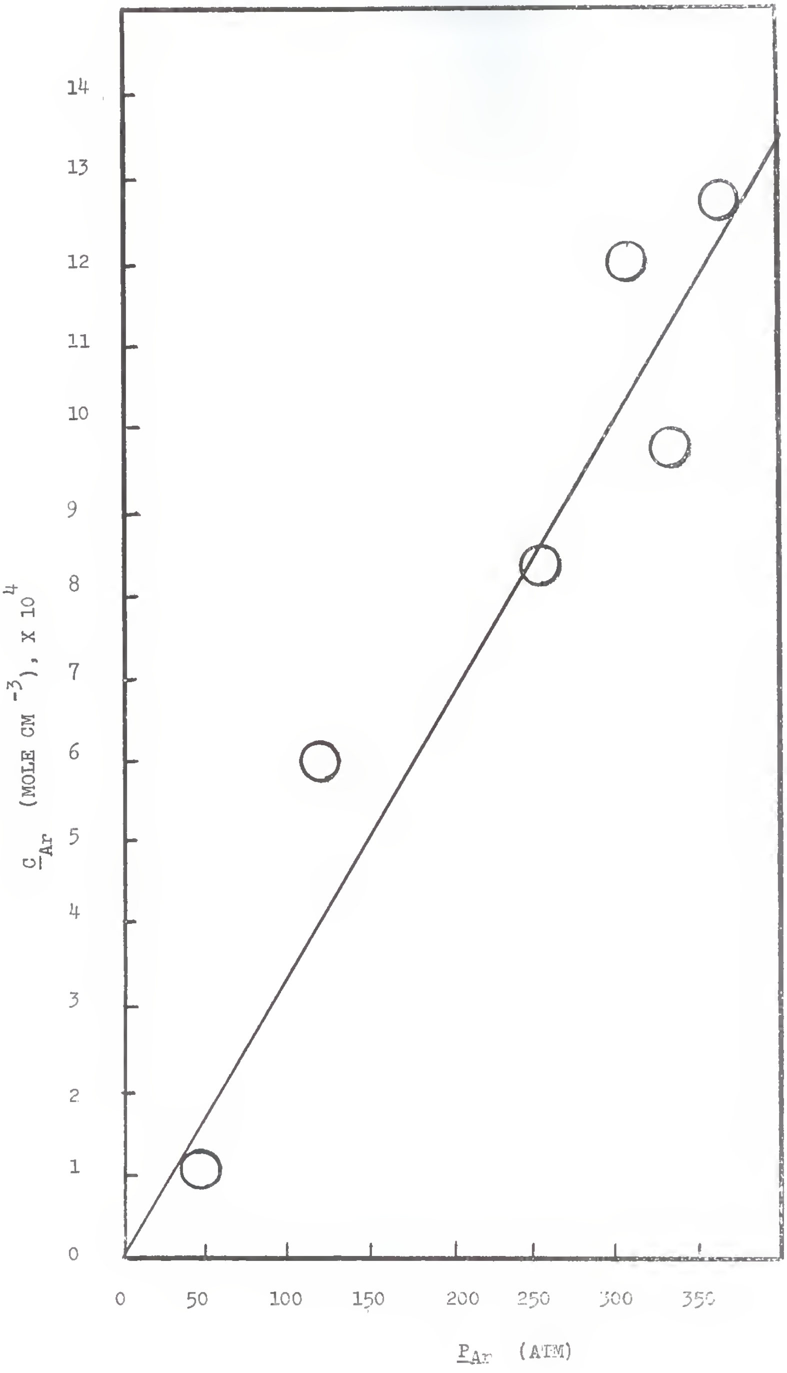
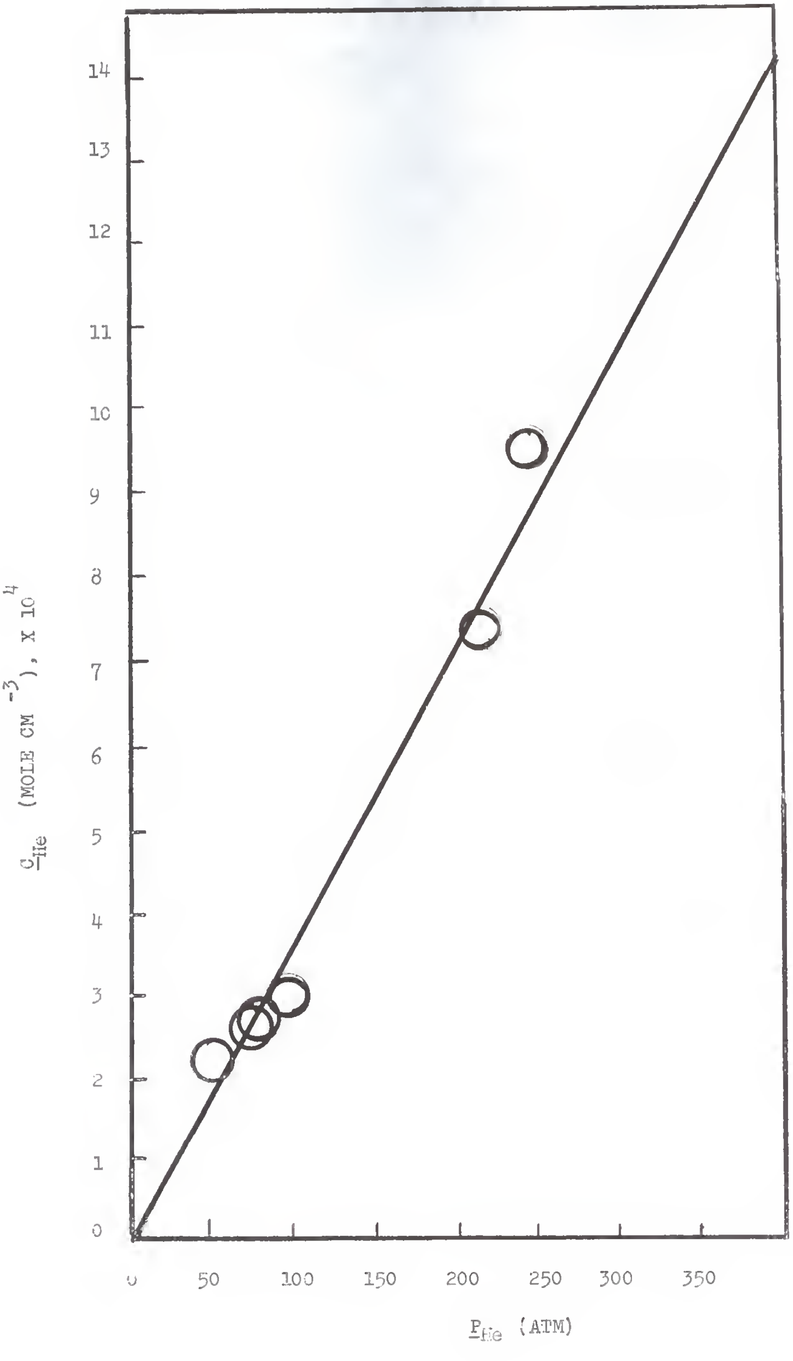

14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
C_Ar (MOLE CM -3), X 10 4
0
50
100
150
200
250
300
350
P_Ar (ATM)

Figure 2. Solubility of Helium in Molten Silver Nitrate at 250°, $\underline{C}_{He}$, *vs*. Saturating Pressures of Helium, $\underline{P}_{He}$.


C_{He} (MOLE CM^{-3}), X 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
50
100
150
200
250
300
350
P_{He} (ATM)

The average slopes calculated from these data yielded the following values for Henry's law constants

$$\underline{K}_{Ar} = (3.35 \pm 0.55) \text{ X } 10^{-6} \text{ moles cm}^{-3} \text{ atm}^{-1} \qquad 15$$

$$\underline{K}_{He} = (3.57 \pm 0.48) \text{ X } 10^{-6} \text{ moles cm}^{-3} \text{ atm}^{-1} \qquad 16$$

where the errors are the probable errors of individual determinations.

II. Conductivities

The conductance measurements were made by taking measurements of the resistance of the molten silver nitrate at various pressures, starting at vacuum (.3 microns), then at 1 atm, after which the pressure was increased in increments of about 80 to 100 atm until the maximum pressure was reached which was the pressure without serious leakage from the system. The gas was then allowed to escape and again the resistance at 1 atm and vacuum were measured to assure that there had been no serious decomposition during the run. The temperature of 250° was chosen only for convenience, for at this temperature one does not have to worry about decomposition or solidification (melting point is 212°) (25).

Tables 3 and 4 are summaries of specific conductance measurements. Figures 3 and 4 are graphs of the specific conductance, k, of the molten salt at 250°, versus the saturating equilibrium pressures of argon and helium, respectively. A striking feature of this study, contrasting with the results obtained by Zybko and Copeland on molten nitrate (19,31), is that the specific conductance, k, at 1 atm is lower than that for vacuum conditions. Although this marked drop in k in the range from vacuum to 1 atm was not reproducible quantitatively (from 0.8370 to 0.8312 $\mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$ in helium run 1, from 0.8370 to 0.8350 $\mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$ in helium run 2, from 0.8370 to 0.8342 $\mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$ in argon run 1, and for argon run 2 not at all) it did occur in many other runs that failed for various reasons. Therefore, due to this consistent behavior in the region of vacuum to 1 atm, we have been forced to the conclusion that this effect on k is probably real, though not quantitatively reproducible. This effect was not indicated by any of the conductance work on sodium nitrate; however, it was not actually sought (19,30).

TABLE 3. Summary of Specific Conductance of Silver Nitrate at 250° Under Argon.[a]

Run 1		Run 2	
Pressure, P_{Ar} atm.	Specific Conductance, k_{Ar}, $ohm^{-1}cm^{-1}$	Pressure, P_{Ar} atm.	Specific Conductance k_{Ar}, ohm^{-1} cm^{-1}
0	0.8370[b]	0	0.8370[b]
1	0.8342	56	0.8326
38	0.8323	55	0.8341
72	0.8298	124	0.8294
140	0.8282	120	0.8296
203	0.8237	180	0.8273
240	0.8221	286	0.8218
315	0.8172	343	0.8188
168	0.8241	315	0.8207
167	0.8241	1	0.8370
1	0.8335	63	0.8332
		61	0.8337

[a] Data are recorded in the order in which they were obtained.

[b] The value of 0.8370 ohm^{-1} cm^{-1} was obtained from the interpolation of Sundheim's and Berlin's data (33). This value gave us the following cell constants: Run 1: C = 298.5 cm^{-1}, and for Run 2: C = 383.0 cm^{-1}.

TABLE 4. Summary of Specific Conductance of Silver Nitrate at 250° Under Helium.[a]

Run 1		Run 2	
Pressure, P_{He}, atm.	Specific Conductance, k_{He}, ohm^{-1} cm^{-1}	Pressure, P_{He}, atm.	Specific Conductance k_{He}, ohm^{-1} cm^{-1}
0	0.8370[b]	0	0.8370[b]
1	0.8312	1	0.8350
37	0.8255	32	0.8322
67	0.8262	63	0.8313
134	0.8207	59	0.8317
225	0.8158	123	0.8274
274	0.8109	156	0.8261
266	0.8118	150	0.8269
350	0.8050	264	0.8208

[a] Data are recorded in the order in which they were obtained.

[b] The value of 0.8370 ohm^{-1} cm^{-1} was obtained from the interpolation of Sundheim's and Berlin's data (26). This value gave us the following cell constants: Run 1: $\underline{C}$ = 298.5 cm^{-1}, and for Run 2: $\underline{C}$ = 383.0 cm^{-1}.

Figure 3-a. Specific Conductance of Molten Silver Nitrate at 250°

Saturated with Argon at Pressures $\underline{P}_{Ar}$. Run 1.

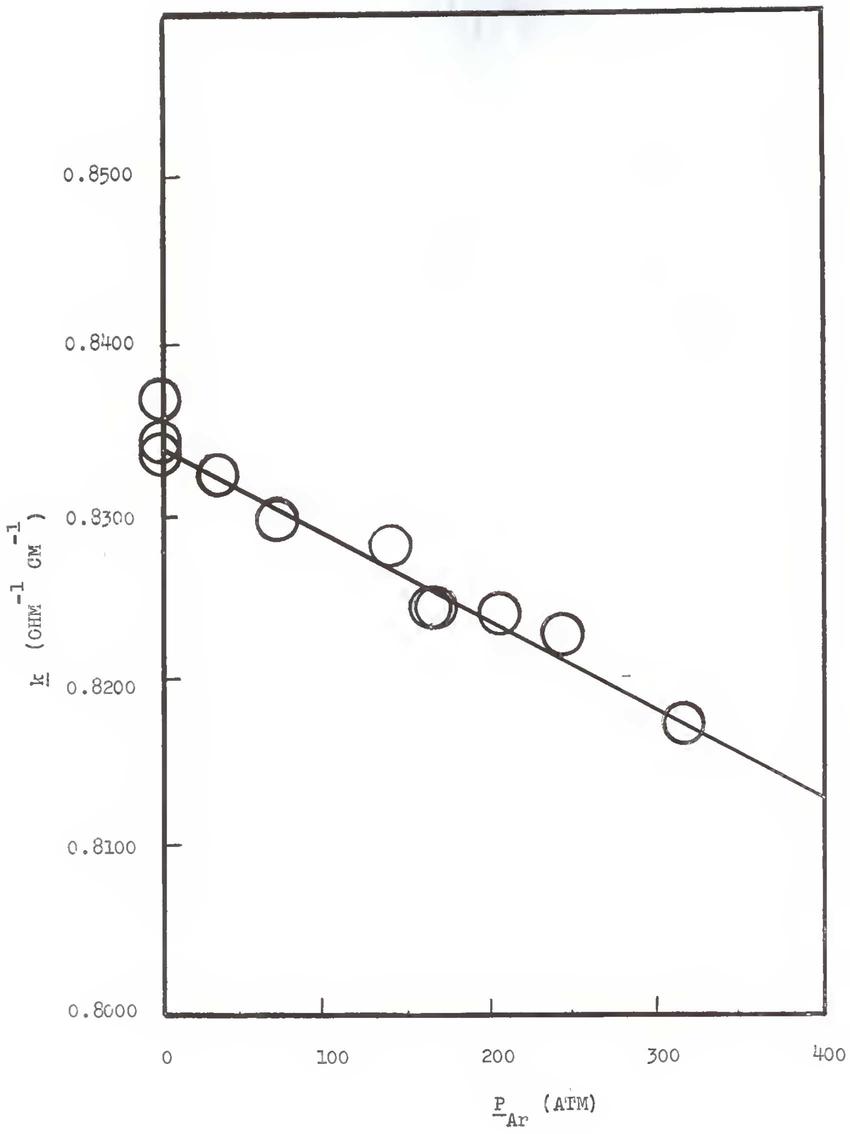

0.8500
0.8400
0.8300
0.8200
0.8100
0.8000
$\underline{k}$ (OHM^{-1} CM^{-1})
0
100
200
300
400
$\underline{P}_{Ar}$ (ATM)

Figure 3-b. Specific Conductance of Molten Silver Nitrate at 250°

Saturated with Argon at Pressures $\underline{P}_{Ar}$. Run 2.

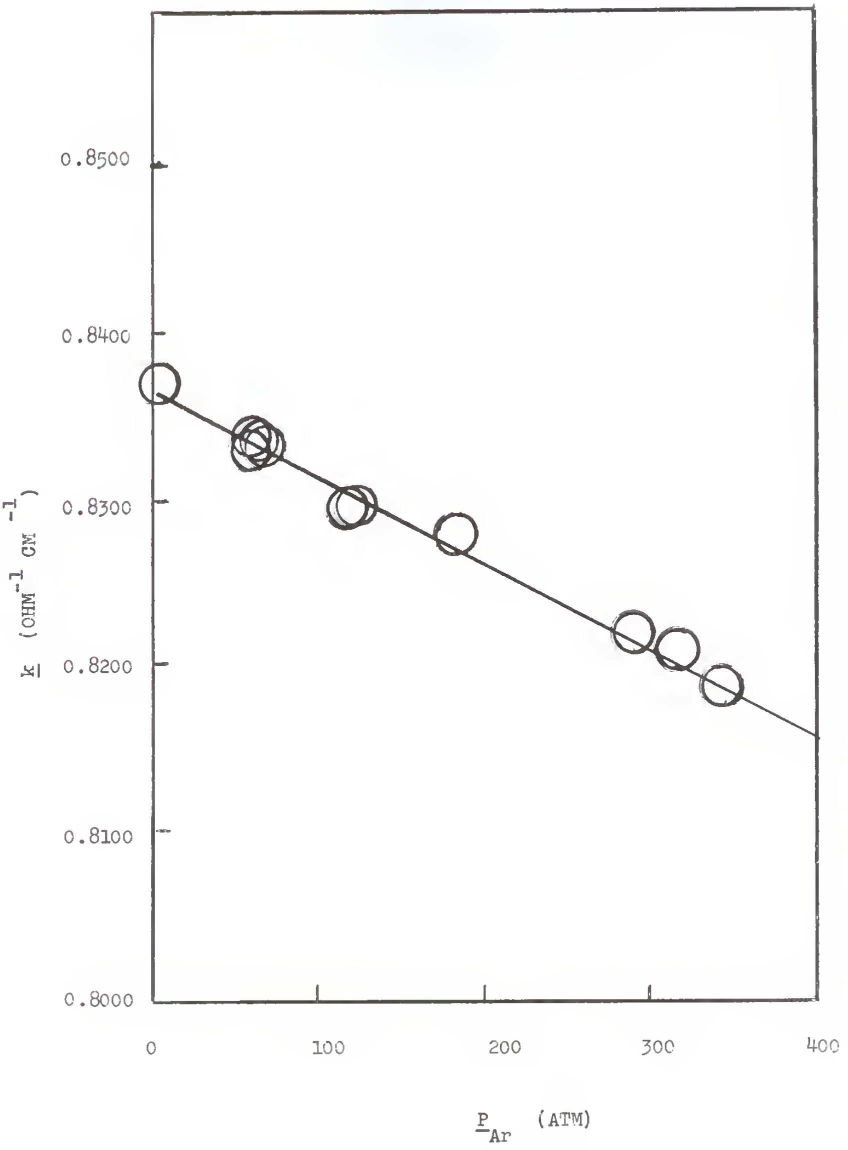

0.8500
0.8400
0.8300
0.8200
0.8100
0.8000
$\underline{k}$ (OHM^{-1} CM^{-1})
0
100
200
300
400
$\underline{P}_{Ar}$ (ATM)

Figure 4-a. Specific Conductance of Molten Silver Nitrate at 250°
Saturated with Helium at Pressures $\underline{P}_{He}$. Run 1.

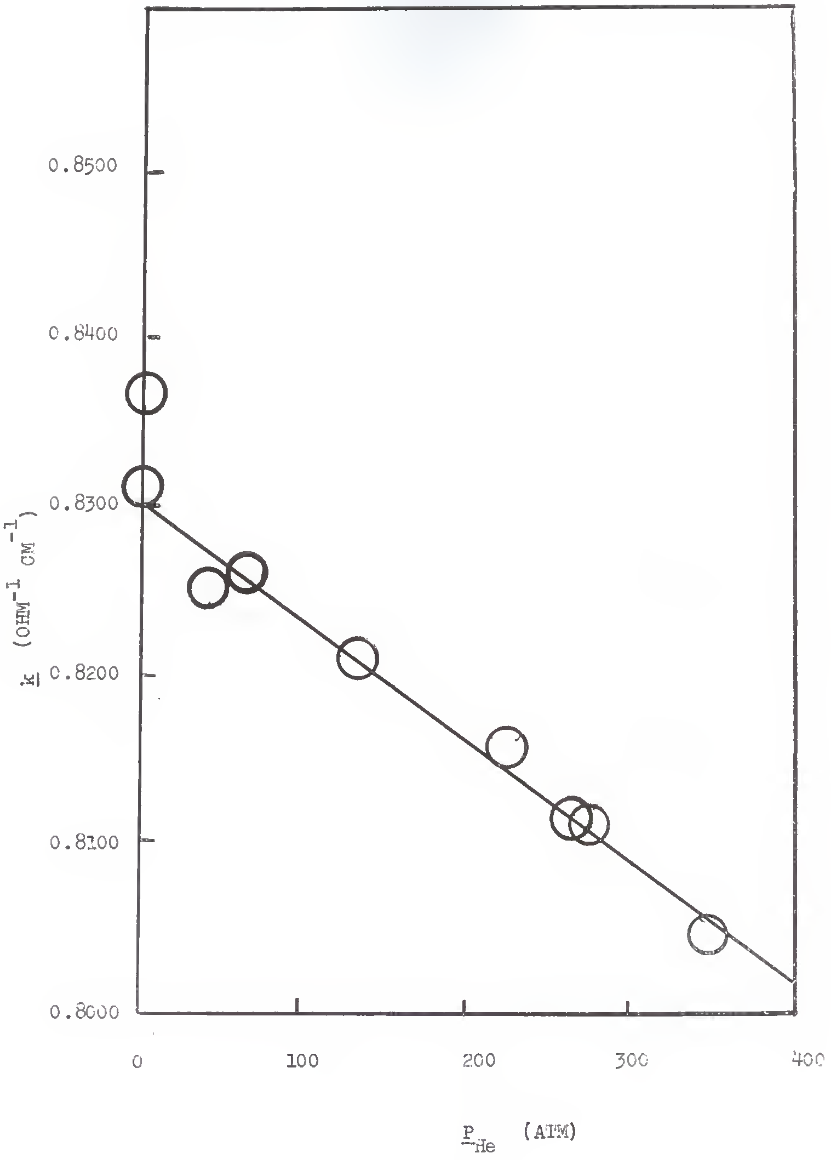
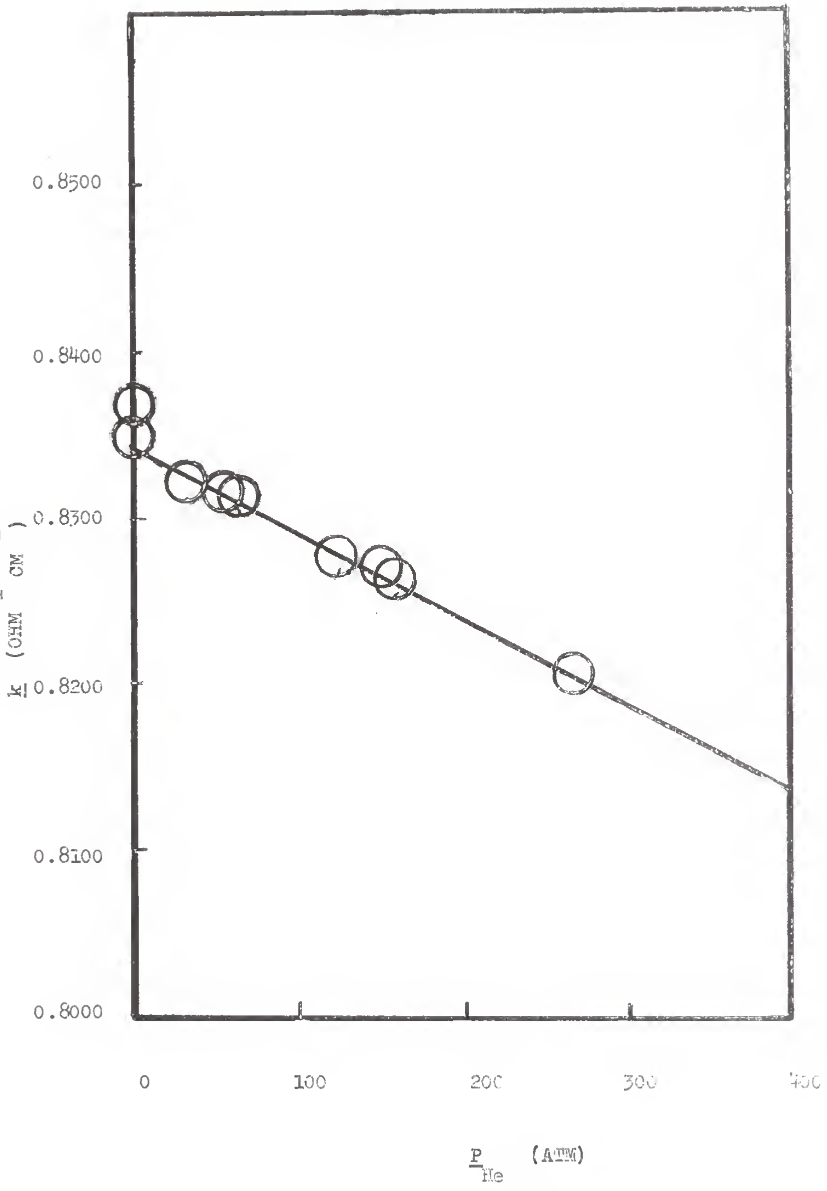

0.8500
0.8400
0.8300
0.8200
0.8100
0.8000
$\underline{k}$ (OHM^{-1} CM^{-1})
0
100
200
300
400
$\underline{P}_{He}$ (ATM)

Figure 4-b. Specific Conductance of Molten Silver Nitrate at 250° Saturated with Helium at Pressures $\underline{P}_{He}$. Run 2.


0.8500
0.8400
0.8300
0.8200
0.8100
0.8000
$\underline{k}$ (OHM^{-1} CM^{-1})
0
100
200
300
400
$\underline{P}_{He}$ (ATM)

Since the aforementioned effect was not quantitatively reproducible, we chose the vacuum measurements as the ones being most common to all of the silver nitrate work, for the determination of the cell constants in all four runs. There are several literature values reported for the specific conductance of silver nitrate. It seems most probable that these measurements were conducted under atmospheric conditions. This, of course, will cause a small error in our cell constant leading to a small error in the slope of the pressure dependence of k of the salt under pressure. The inconsistencies of the literature values may be related to the previously undetected effect just reported here. A value of 0.8370 ohm^{-1} cm^{-1} (26) was used to calculate the cell constant at the common zero pressure resistance value for each run. The reason for using this value is that it seemed the most reliable, if for no other reason that it contains more significant figures than any of the other reported values. The least squares analyses of the four runs, where the zero pressure measurements were excluded, gave the following empirical straight line equations for k versus gas pressure, P, in atm

Helium Run 1. $k_{He} = (0.8302 \pm 0.0005)-(7.01 \pm 0.24) \times 10^{-5} P_{He}$ ohm^{-1}cm^{-1} 17

Run 2. $k_{He} = (0.8345 \pm 0.0002)-(5.28 \pm 0.12) \times 10^{-5} P_{He}$ ohm^{-1}cm^{-1} 18

Argon Run 1. $k_{Ar} = (0.8340 \pm 0.0003)-(5.24 \pm 0.18) \times 10^{-5} P_{Ar}$ ohm^{-1}cm^{-1} 19

Run 2. $k_{Ar} = (0.8364 \pm 0.0002)-(5.11 \pm 0.09) \times 10^{-5} P_{Ar}$ ohm^{-1} cm^{-1} 20

The errors are the least squares probable errors. In equations 17-19 it is seen that the least squares intercepts are noticeably below that of the zero pressure point of 0.8370 ohm^{-1} cm^{-1}, and that of equation 20 is just below this point.

DISCUSSION

We discerned three unusual differences in the behavior of the silver nitrate system as compared to the sodium nitrate studies, these being (a) the apparent and unusual tendency for the specific conductance of silver nitrate to decrease from vacuum conditions (.3 microns) to saturation at 1 atm; (b) the effective equality of the pressure coefficients of the specific conductance for both helium and argon (whereas in the sodium nitrate study the argon had a pressure dependency of over twice that of helium); and (c) the equality, within error, of the solubilities of helium and argon in silver nitrate, in contrast to their inequality in sodium nitrate. Also, both gases were found to be more soluble in the silver nitrate melt than they were in the sodium nitrate melt.

Duke and Fleming (27) pointed out the variances in the literature values of specific conductance for silver nitrate, and consequently, they redetermined this property. Thus, some of the values one can find for k for silver nitrate at 250° in the literature are: 0.85 $\text{ohm}^{-1}\ \text{cm}^{-1}$ (28), 0.840 $\text{ohm}^{-1}\ \text{cm}^{-1}$ (29), 0.836 $\text{ohm}^{-1}\ \text{cm}^{-1}$ (27), and 0.8370 $\text{ohm}^{-1}\ \text{cm}^{-1}$ (26). As mentioned previously, we assumed that these values were obtained under atmospheric conditions. Since the observed drop in k occurred between vacuum and 1 atm, it may be that this qualitatively-observed effect could, in part at least, be causing these variances. The fusion of silver nitrate by these workers may have been carried out under such conditions that equilibrium may not have existed with the pressure of air used in the experiments. This argument can be invoked to give a possible explanation as to why the drop in k was not quantitatively reproducible in our work; if during the evacuation before fusion, a small or even trace amount of some gas was occluded in the system, it could possibly have a profound effect upon the conductance determined during the "vacuum" measurement. In the helium study, it appeared that this gas was very strongly occluded at pressures less than 1 atm, for even prolonged pumping-out did not return the resistance under vacuum to that which was measured in the beginning of the run. This tendency for gas occlusion did not seem to be as great for argon; and it was possible in one of the two runs to reproduce the vacuum measurements of resistance.

We would like to suggest two possible mechanisms to account for this drop in $\underline{k}$ between vacuum and 1 atm. The first is that possibly the gas dissolving at low pressures is doing so by occupying some of the free volume, thereby removing part of the latter from the conductance mechanism involving, in part, some sort of ionic "jumping". After such amounts of free volume which are available to these gas molecules are filled, the additional and also gradual decrease of $\underline{k}$ with higher gas saturation pressures may be the result of a dilution process, as postulated by Zybko and Copeland (30) in their studies with fused sodium nitrate. This hypothesis, which utilizes the liquid free volume for ion-jumping similar to that suggested by Bockris and Richards (33) or Cohen and Turnbull (9), involves a polyionic movement, where the mobile particles are not only ions but groups of ions. Thus, in this model the initial gas solubility at low pressures is due to the occupancy of some of the liquid free volume "cells" of favorable spatial extent by the gas with negligible expenditure of energy. These initially dissolved gas molecules would therefore remove from the system a portion of the liquid free volume used for conductance, thereby leading to a decrease in conductance between vacuum and 1 atm. The additional solubility of the gas at higher pressures is thus due to the gas molecules endothermally creating their own holes in the melt, thus diluting the salt. Needless to say when an electrolyte is diluted its specific conductance is lowered.

The second possibility is that of trace electronic conductance in the melt; that is, the first "few" molecules of gas may act as scattering centers for electrons, thus nullifying the electronic conductance of the system. The dilution mechanism would again prevail at higher pressures and gas solubilities.

The similarity of the pressure dependency of k in silver nitrate for both argon and helium have led us to the conclusion that there is no measureable difference in the effects of either gas pressure or solubility on the specific conductance in this system. This contrasts with the pressure dependence of k for sodium nitrate [$(-9.19 \pm 0.25) \times 10^{-5}$ ohm^{-1} cm^{-1} atm^{-1}, $(-1.94 \pm 0.06) \times 10^{-4}$ ohm^{-1} cm^{-1} atm^{-1}] , where the argon caused more than twice the pressure dependence than did helium. Also, it was found that for the silver nitrate system the gases caused a similar, but smaller pressure dependence than did helium in sodium nitrate.

Similarly we must conclude from the closeness of the Henry's law constants for both gases in silver nitrate that their solubilities are the same within error, in the pressure range employed in this study. The Henry's law constants for helium and argon in sodium nitrate at 369° are smaller than those in silver nitrate at 250° [for $NaNO_3$, $K_{Ar} = (1.72 \pm 0.17) \times 10^{-6}$ mole cm^{-3} atm^{-1}, $K_{He} = (2.27 \pm 0.07) \times 10^{-6}$ mole cm^{-3} atm^{-1}] (30). At 400 atm, for example, it was found that helium had a solubility of 0.058 mole fraction in silver nitrate, as compared to 0.039 mole fraction in sodium nitrate (19). This is in poor agreement with the model of Blander, Grimes, Smith and Watson (31), where a noble gas should be less soluble in a fused salt of higher surface tension at a given temperature, and more soluble in a salt of a given surface tension at a higher temperature. The surface tension at 250° of silver nitrate is higher than that of sodium nitrate at 369° 149.0 dynes cm^{-1} and 113.5 dynes cm^{-1}, respectively (32) . Thus, the silver nitrate system is a poor example for the above model for noble gas solubility for two reasons: temperature and surface tension. At this time we have no explanation for this behavior of helium and argon in the molten silver nitrate system.

CONCLUSION

We conclude that the evidence for the unusual drop in the specific conductance of fused silver nitrate in the region from vacuum to 1 atm is real. Also, the gradual decrease in conductance above 1 atm is probably due to a dilution of the melt by the gas. We also believe that the nature of the noble gas is unimportant in this system, since both pressure dependences of gas solubility and conductance of silver nitrate were equal within experimental error for both helium and argon.

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EFFECT OF INERT GAS PRESSURE AND SOLUBILITY ON ELECTRICAL CONDUCTANCE OF FUSED $AgNO_3$

by

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These experiments, which measured the affects of pressure and solubility upon electrical conductance of molten $AgNO_3$, were done for the purpose of helping to elucidate the nature of molten salts. A Parr pressure bomb, similar to that used by Zybko and Copeland (30) in their study of fused sodium nitrate, was used; the bomb contained platinum conductance electrodes and thermocouples for the conductance work and only thermocouples in the solubility work.

The solubilities of both argon and helium in fused silver nitrate at 250° were determined at pressures up to 375 and 247 atm, respectively. The Henry's law constants are

$$\underline{K}_{Ar} = (3.35 \pm 0.55) \times 10^{-6} \text{ mole cm}^{-3} \text{ atm}^{-1}$$

$$\underline{K}_{He} = (3.57 \pm 0.48) \times 10^{-6} \text{ mole cm}^{-3} \text{ atm}^{-1}$$

Due to the similarity of the Henry's law constants for both argon and helium, we concluded that the two gases were equally soluble in the melt.

The specific conductances, $\underline{k}$, of silver nitrate at 250° were also determined for the two gases and gave the following results for duplicate runs

1. $\underline{k}_{Ar} = (0.8340 \pm 0.0003)-(5.24 \pm 0.18) \times 10^{-5}\ \underline{P}_{Ar}$ ohm^{-1} cm^{-1}
2. $\underline{k}_{Ar} = (0.8364 \pm 0.0002)-(5.11 \pm 0.09) \times 10^{-5}\ \underline{P}_{Ar}$ ohm^{-1} cm^{-1}
1. $\underline{k}_{He} = (0.8302 \pm 0.0005)-(7.01 \pm 0.24) \times 10^{-5}\ \underline{P}_{He}$ ohm^{-1} cm^{-1}
2. $\underline{k}_{He} = (0.8345 \pm 0.0002)-(5.28 \pm 0.12) \times 10^{-5}\ \underline{P}_{He}$ ohm^{-1} cm^{-1}

where pressures are in atm. An additional observation made in the conductance study was a marked drop in conductance between vacuum and 1 atm in three out of the four runs (from 0.8370 to 0.8312 ohm^{-1} cm^{-1} in helium run 1, from 0.8370 to 0.8350 ohm^{-1} cm^{-1} in helium run 2, from 0.8370 to 0.8342 ohm^{-1} cm^{-1} in argon run 1, and not at all in argon run 2).

Due to the similarity of the pressure dependency for both gases in the conductance and solubility work, we concluded that the nature of these noble gases, within experimental limits, is unimportant in this system. We have proposed two possible explanations for the conductance drop in the range between vacuum and 1 atm. The first involves the concept of liquid free volume where a part of the free volume is removed from the system by occupancy by the first "few" molecules which dissolve in the melt. After the liquid free volume "cells" of favorable spatial extent are occupied, the gas, at higher pressures and concentrations, dissolves principally by diluting the melt, as postulated in earlier work (30). The second possibility is that of trace electronic conductance, where the first "few" molecules of gas may act as scattering centers for such electrons, thus effectively eliminating the electronic contribution to $\underline{k}$. Here, again, the dilution mechanism would prevail at higher pressures and gas solubilities.